



# Microplastics Method Development – Case Study for Wastewater Effluent Environmental Measurement Symposium 11 August 2016

# Plastics vs microplastics

- ▶ Microplastic as emerging contaminant
- ▶ Lack of definition
- ▶ Lack of standardized method
- ▶ No published method for wastewater matrix

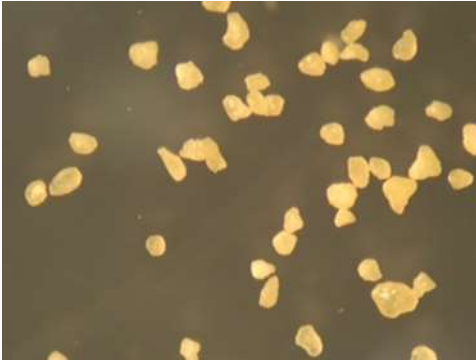


# Microplastic bead ban – Federal

- Microbead-Free Waters Act of 2015
- Prohibits sale/distribution of rinse-off cosmetics containing plastic microbeads
- Includes toothpaste
- Definition of microplastic:
  - *...any solid plastic particle that is less than five mm in size and intended to be used to exfoliate or cleanse the human body or any part thereof*
- Manufacturing ban starts July 1, 2017
- Sales ban starts July 1, 2018
- Non-prescription drugs – one year lag



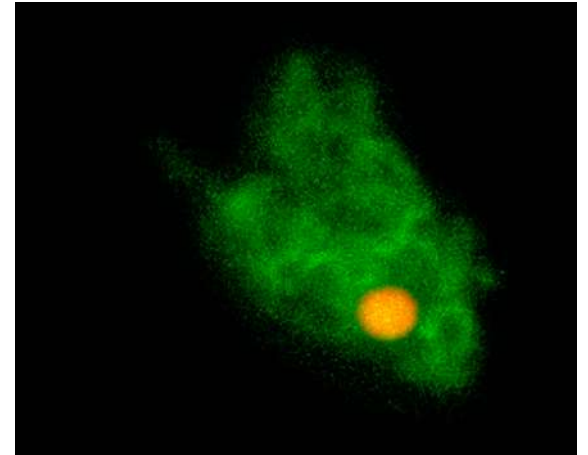
# Microplastic bead ban – CA



- ▶ California ban:
  - AB 888: Plastic microbeads nuisance prevention law
  - Effective January 1, 2020
  - Exempts promotional products containing less than 1 ppm by weight of microbeads
  - Definition of plastic microbeads:
    - *“...Intentionally added solid plastic particle measuring 5mm or less in every dimension”*

# The pollutant

- ▶ Found in aquatic environment
- ▶ Health effects:
  - Accumulation and blockage
  - Chemicals in the polymer
  - Sorbed pollutants
- ▶ Few environmentally relevant experimental data available
- ▶ Call for action before fully understood



# Sources and pathways

- ▶ Sources
  - Urban trash
  - Synthetic clothes and fabrics
  - Microbeads in personal care products
- ▶ Pathways to aquatic environment
  - Storm water
  - Rivers
  - Wind
  - Wastewater

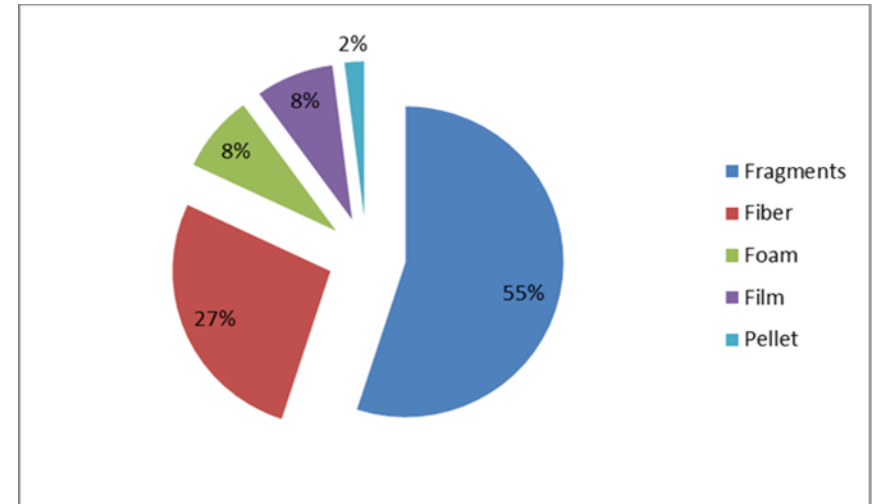
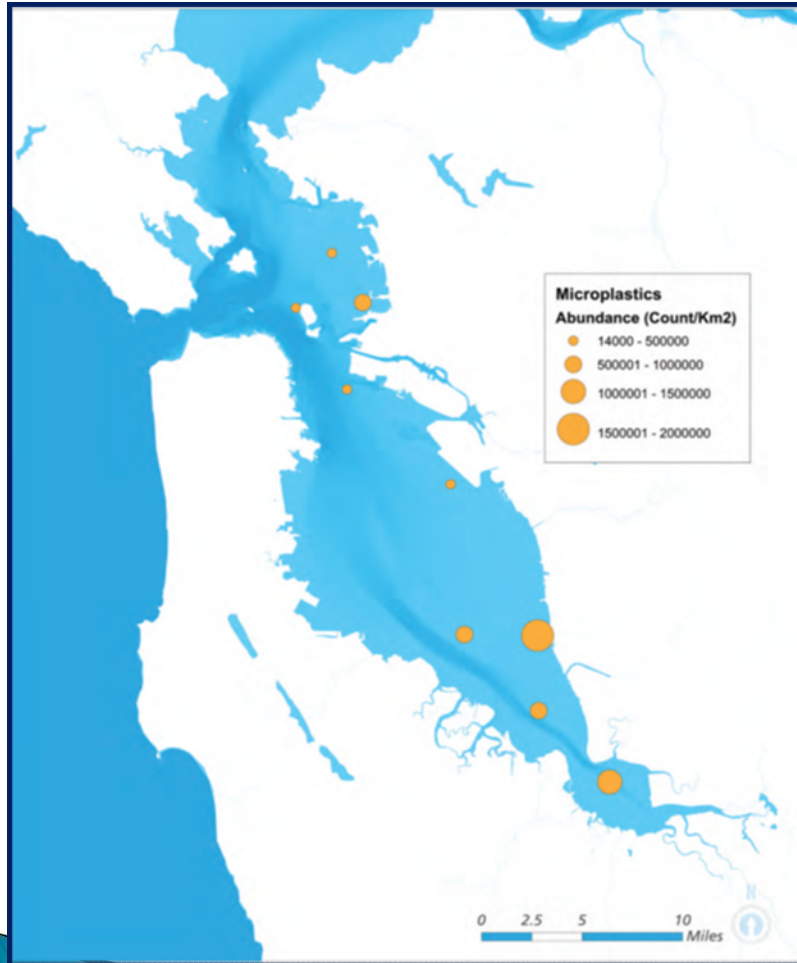


# Microplastics in SF Bay

- ▶ San Francisco Estuary Institute (SFEI)
- ▶ Regional Monitoring Program (RMP)
- ▶ Bay Area Clean Water Agencies (BACWA)
- ▶ Emerging contaminant workgroup
  - Microplastics in the Bay
  - Microplastics in the WWTP effluent



# SFEI report on the SF Bay

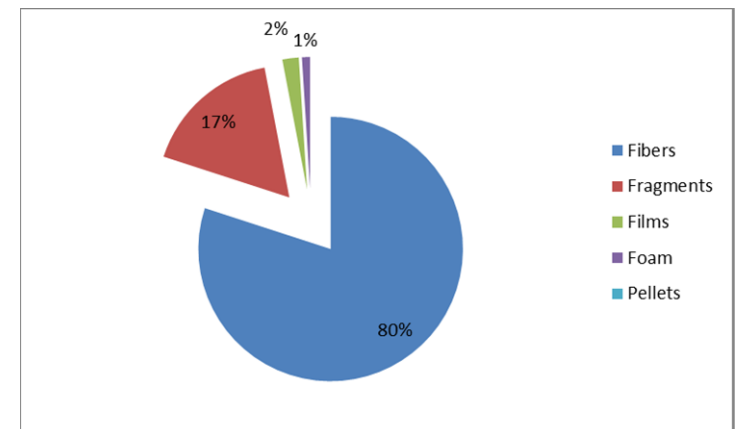


# SFEI report – WWTP

- 8 WWTP volunteered
- One sample collected per WWTP
- Sample size – 2 hour composite
- Did not differentiate between microparticles and microplastic particles

WWTP	PARTICLES/ GALLON	PARTICLES/ DAY
San Jose-Santa Clara	0.18	15,000,000
East Bay MUD	0.27	12,000,000
Palo Alto	0.48	9,600,000
Central Contra Costa	0.27	8,100,000
Fairfield-Suisun	0.35	4,100,000
EBDA/San Leandro	0.082	4,100,000
San Mateo	0.24	2,000,000
SFO (sanitary plant)	0.74	460,000
Average	0.33 ± 0.19	6,990,000 ± 4,700,000

**TABLE 1.** Microplastic levels in Bay WWTP effluent



# Wastewater nexus



- ▶ WWTP remove >95%
- ▶ Attempts to verify data
- ▶ Bay Area Clean Water Agencies (BACWA) Exec Board requested verification
- ▶ Microplastics vs. microparticles

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**TABLE 1.** Microplastic levels in Bay WWTP effluent



# The assignment and the goal

To characterize and quantify microplastics in wastewater effluent

- ▶ BACWA microplastics workgroup goal
  - Routinely performed
    - not too expensive
    - not too complex
  - Robust QA/QC criteria
  - Inter-laboratory reproducibility
  - Complete documentation and transparency
  - Provide useful information for decision making



# First attempts

- ▶ No existing method specific for wastewater effluent
- ▶ NOAA method (July 2015) “Laboratory methods for the analysis of microplastics in the marine environment: recommendation for quantifying synthetic particles in water and sediments”
- ▶ Needed a definition, and created one:

*Material that passes through a 5mm sieve but retained by 0.125 mm sieve; withstands oxidation step and then confirmed as plastic.*



# Sampling methods, sample size

- ▶ Grab vs. composite
- ▶ Duration of composite sampling
- ▶ Flow rate
- ▶ Sampling location
- ▶ Sieve arrangement



# After 24 hours

5 mm sieve



1 mm sieve



0.355 mm sieve



0.125 mm sieve

# 49 hour composite samples (1698 gallons)



24 hour composite samples (1440 gallons; from 0.355 mm sieve)

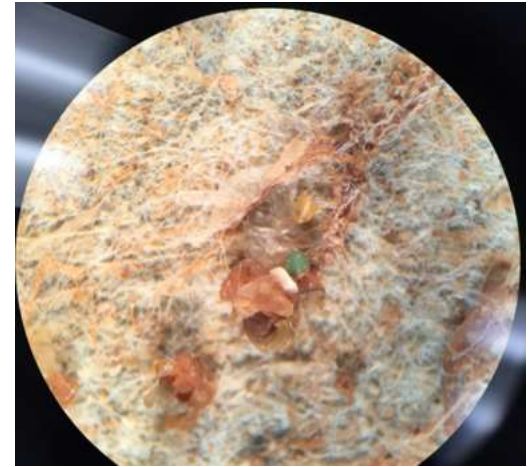


# Sample preparation – Wet Peroxide Oxidation (WPO)

- ▶ Add 20 mL 0.05M  $\text{FeSO}_4$  solution and 20 mL 30%  $\text{H}_2\text{O}_2$ 
  - $\text{FeSO}_4$ : 7.5g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dissolved in 500 ml DI water; add 3 ml  $\text{H}_2\text{SO}_4$
- ▶ Let it stand for 5 minutes
- ▶ Add stir bar and place on a hot plate (75C) at 200–500 rpm for 20 min
- ▶ Repeat as necessary
- ▶ Cool down
- ▶ Filter through Buchner funnel (45mm 0.8 $\mu\text{m}$  membrane filter)
- ▶ Rinse the beaker with DI  $\text{H}_2\text{O}$  two times
- ▶ Filter the rinsate

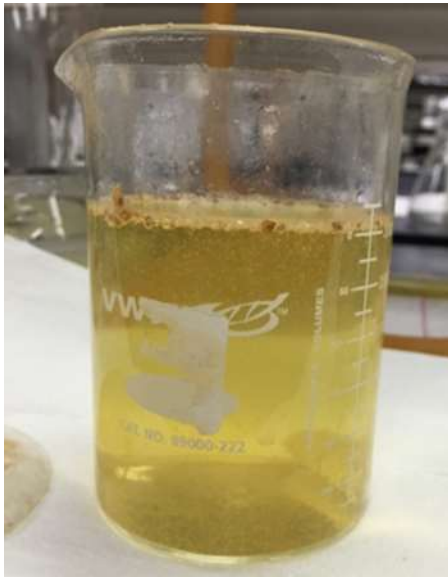


# After WPO

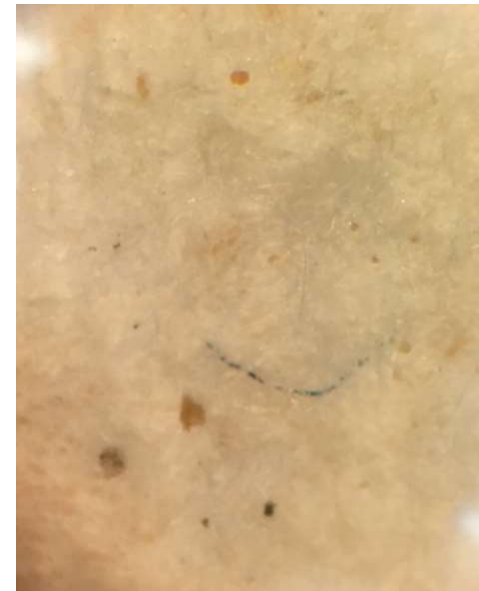


Method needs refinement to remove interferences

# Density separation



Top layer

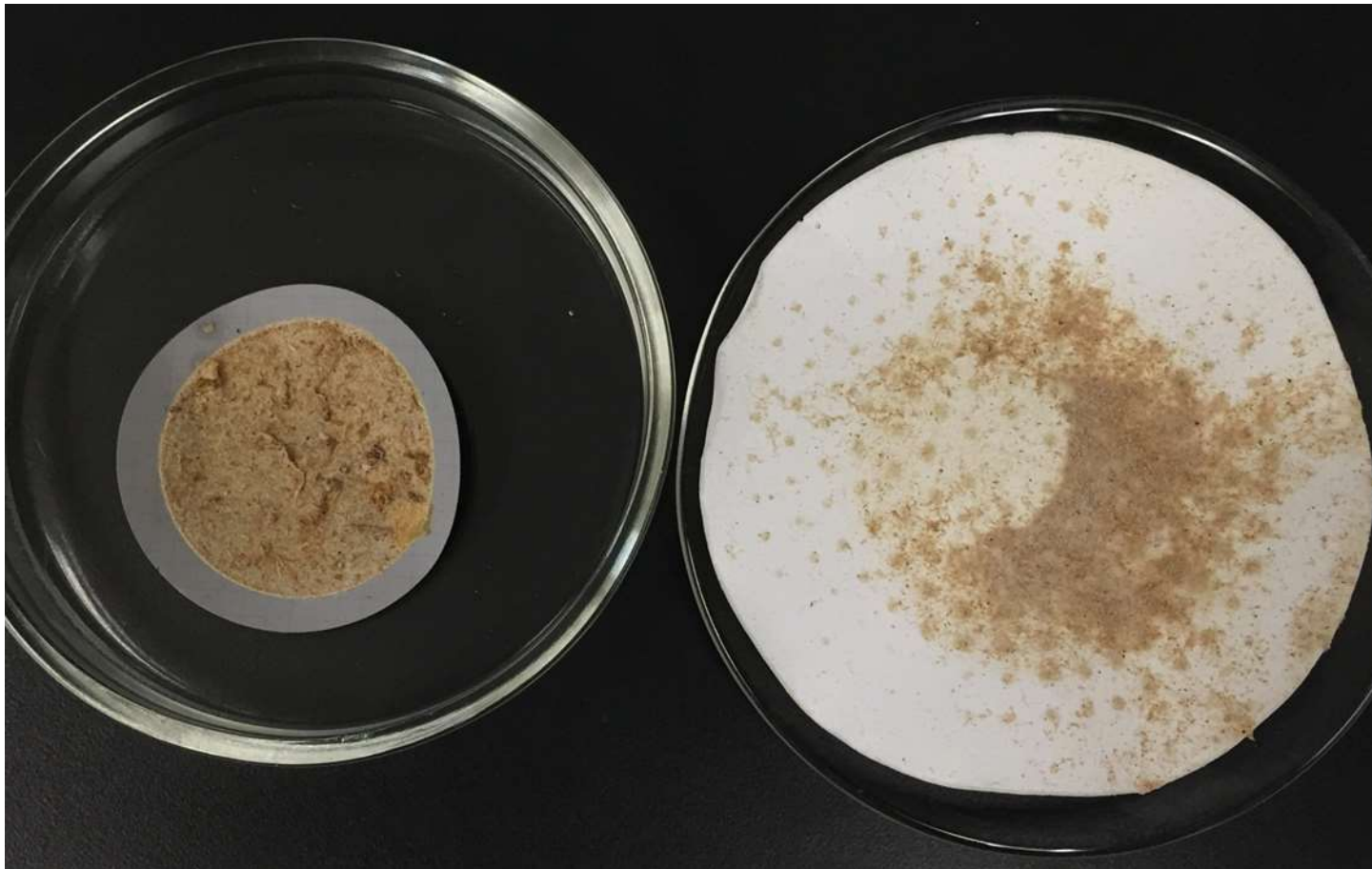


Bottom Layer

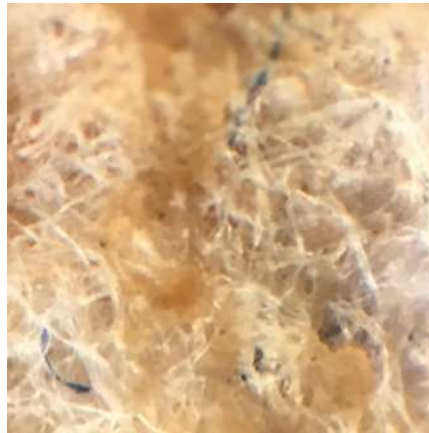
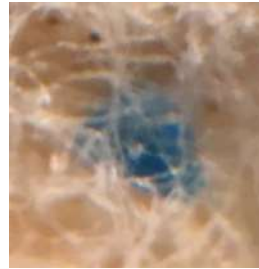
Density separation with saturated NaCl applicable to marine environment samples, not for wastewater effluent.



# 47 mm vs 90 mm membrane filter

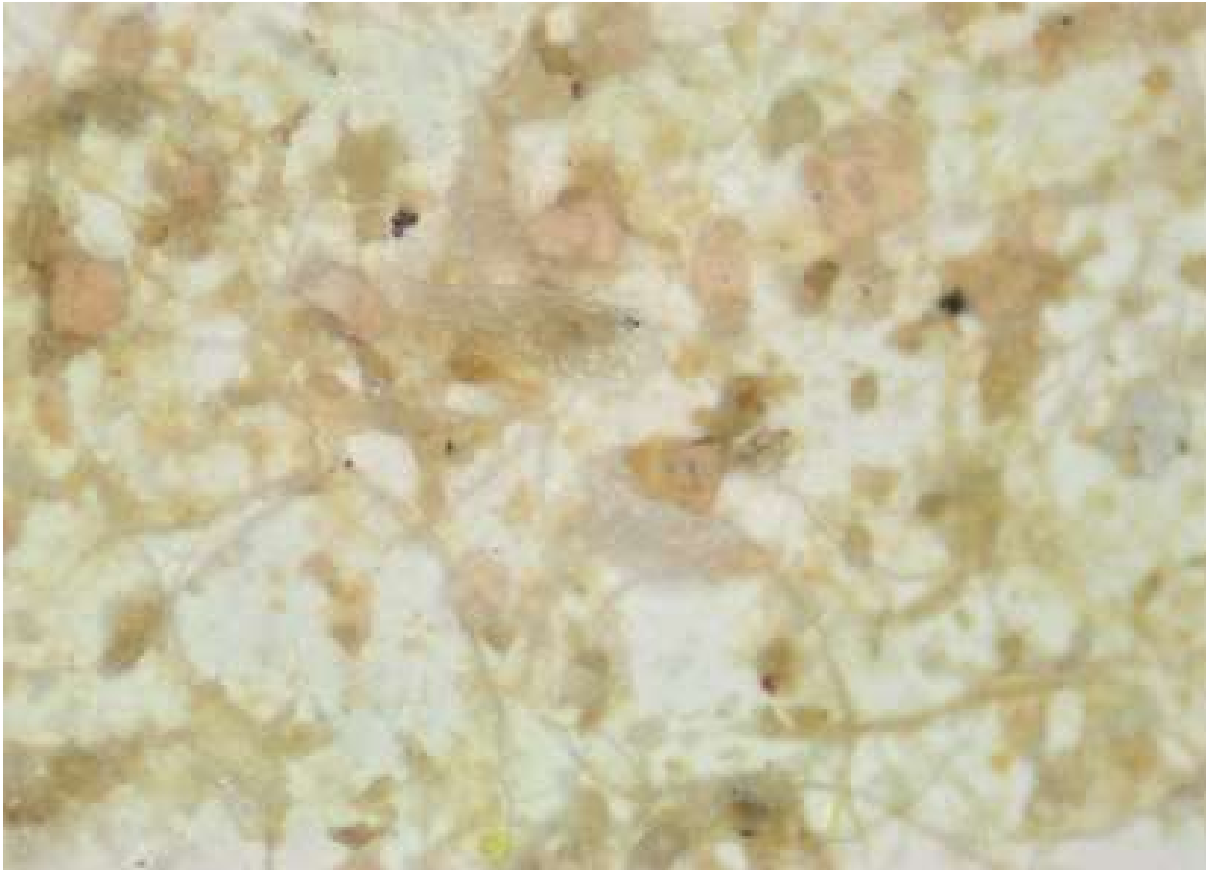


# Increasing WPO

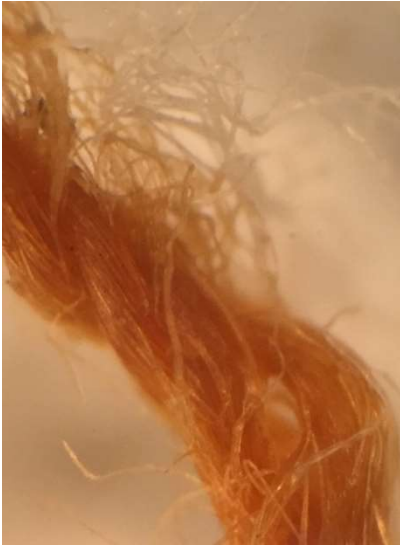


# What is in the background?

## Cellulose fibers & grease balls



# DI Water spiked with non-microplastics



Clothing



Clothing



Human hair

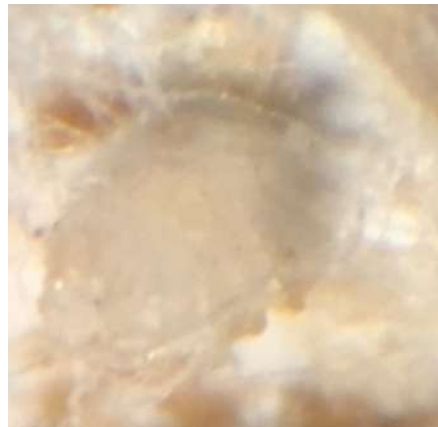
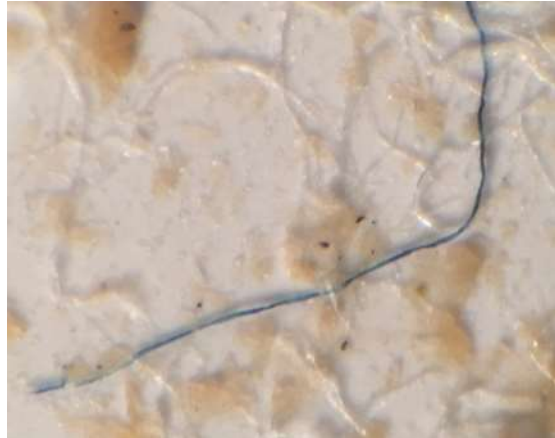


Toilet paper

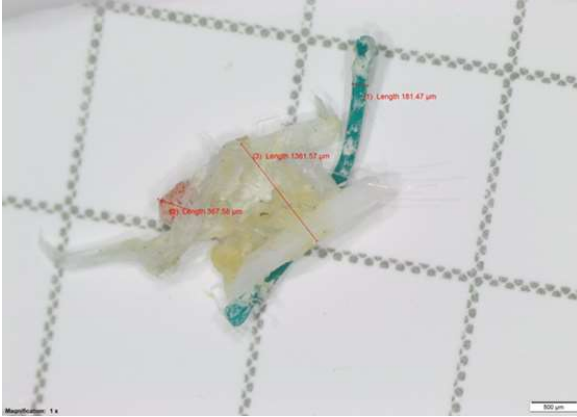


Cigarette filter

# Warm methanol rinse

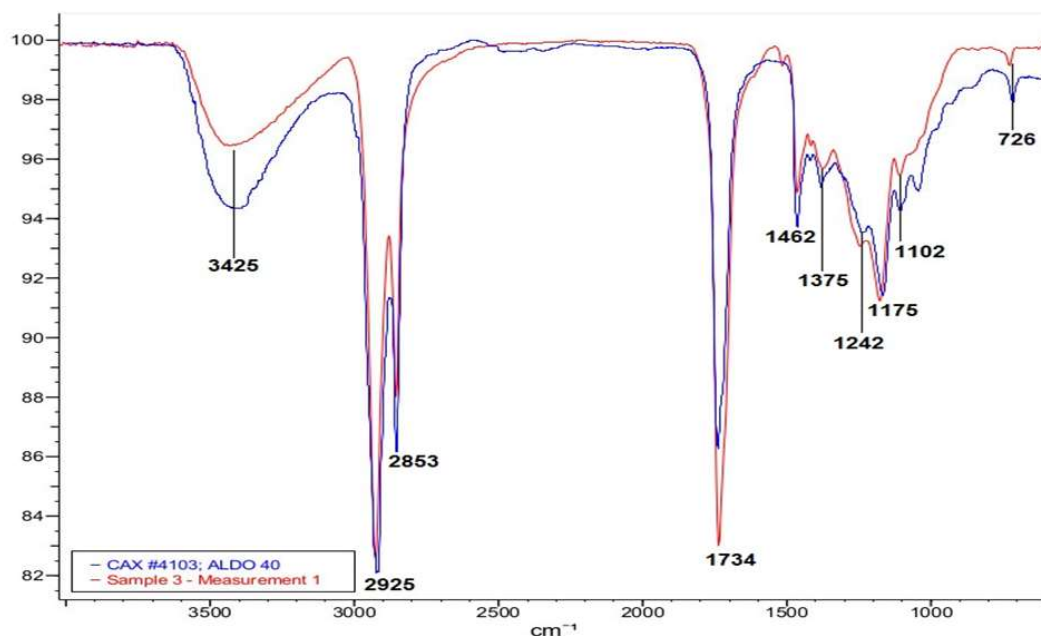


# Modified procedure – Hexane rinse

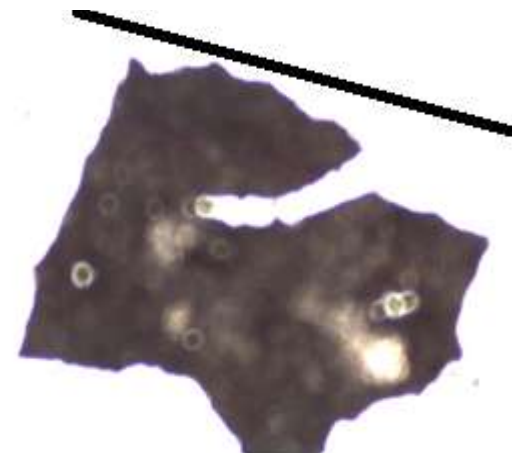


1. WPO
2. Transfer content of beaker to 0.125 mm sieve
3. Wash with gentle stream of water and collect all solids in a corner
4. Rinse solids with 20 ml hexane 3 times
5. Transfer solids back to beaker and start another WPO
6. Repeat steps 2–5 if needed
7. Filter through membrane filter
8. Microscopic exam and FTIR confirmation

# Glyceryl oleo stearate



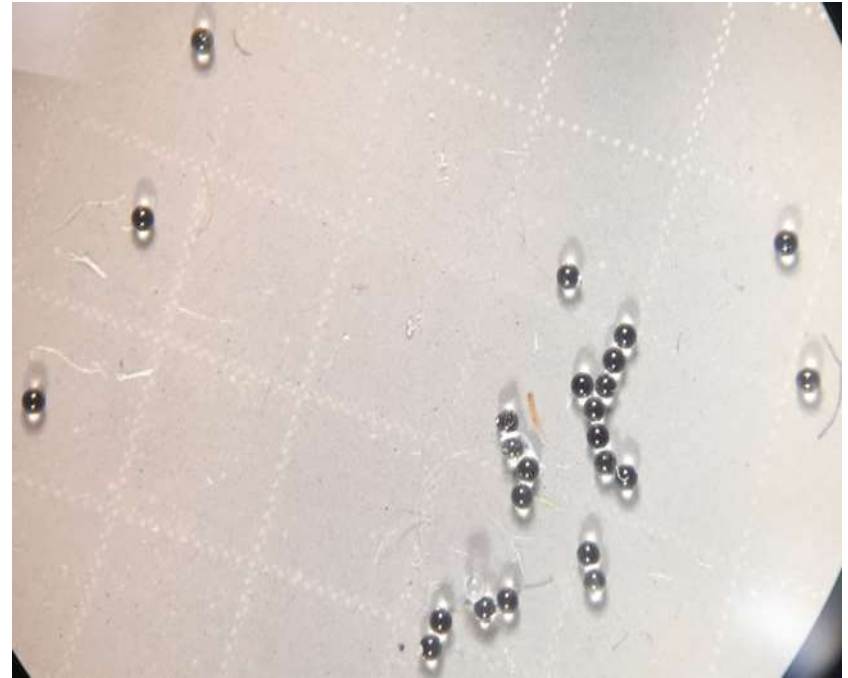
Name	Value
Name	ALDO 40
Comments	Chemical Description= GLYCERYL OLEO STEARATE Description= EMULSIFYING AGENT
Source of Sample	GLYCO CHEMICALS, INC.
Technique	FILM



# Blank spike recovery 89%



27 beads



24 beads



# MicroFTIR confirmation



Polyacrylonitrile



Cotton



# 1 mm sieve (collected 04/13/16)



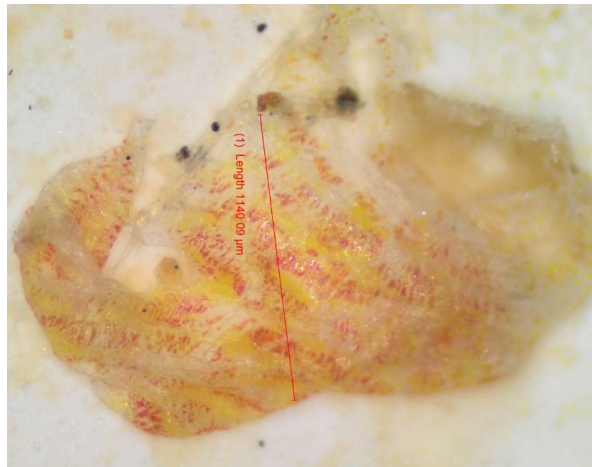
Polyethylene



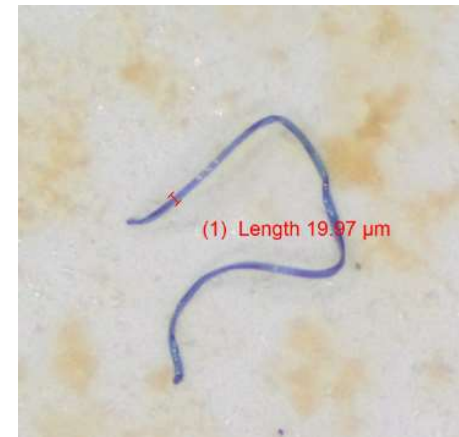
Polyethylene



Polyethylene



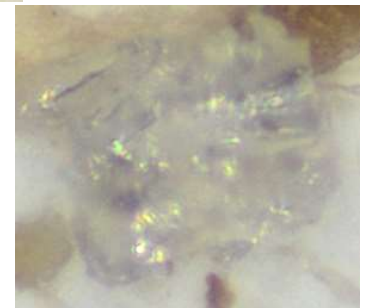
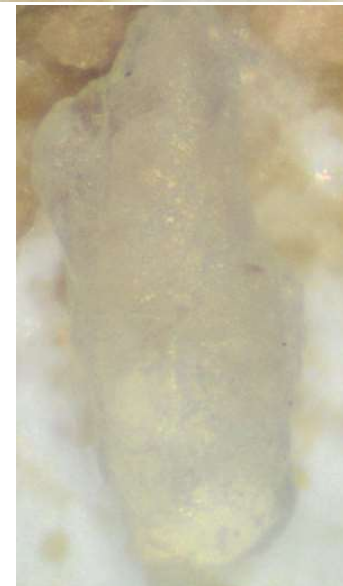
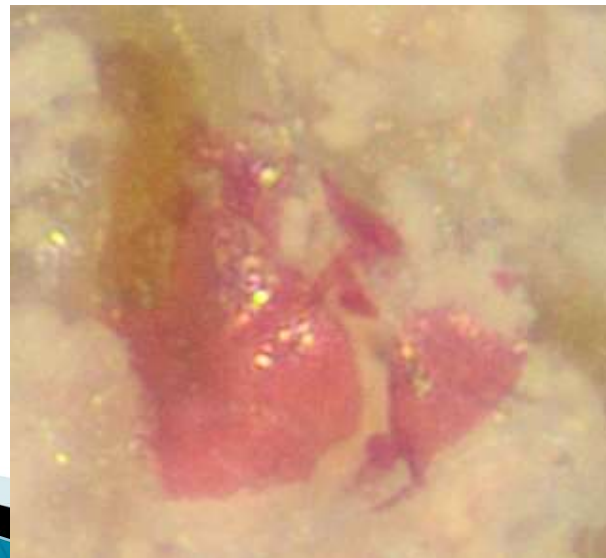
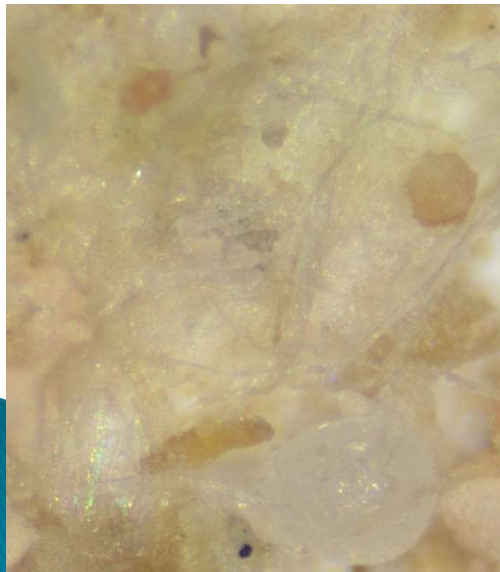
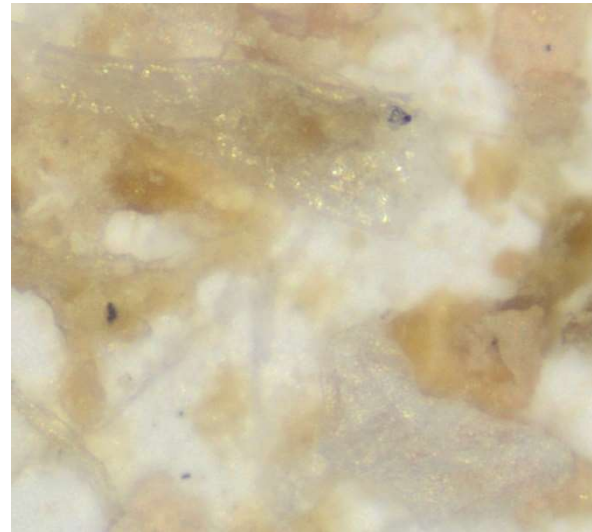
Polyethylene



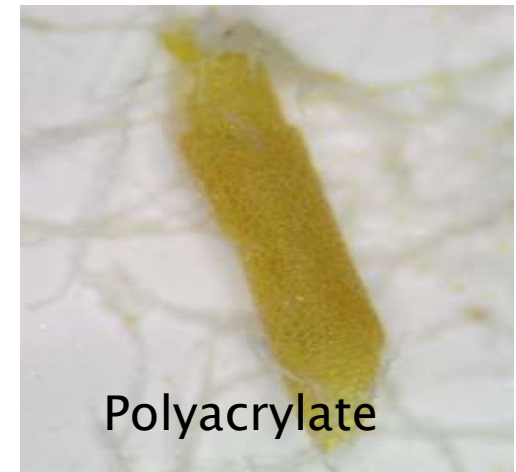
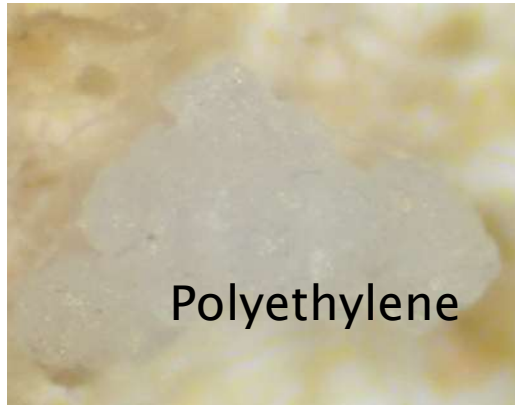
Acrylic fiber

Identified by Thermo 5/24/16

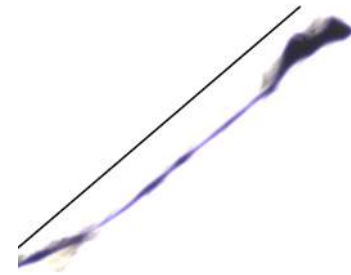
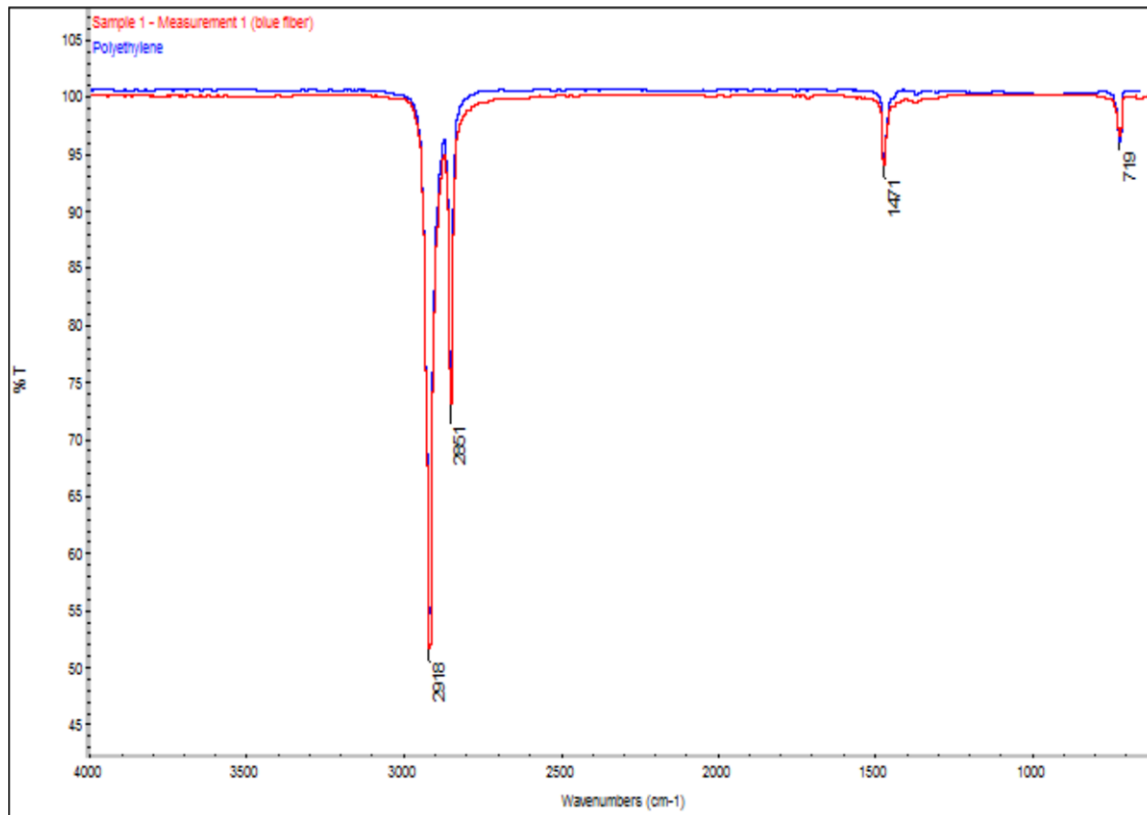
# Suspected polyethylene films (355 $\mu\text{m}$ sieve)



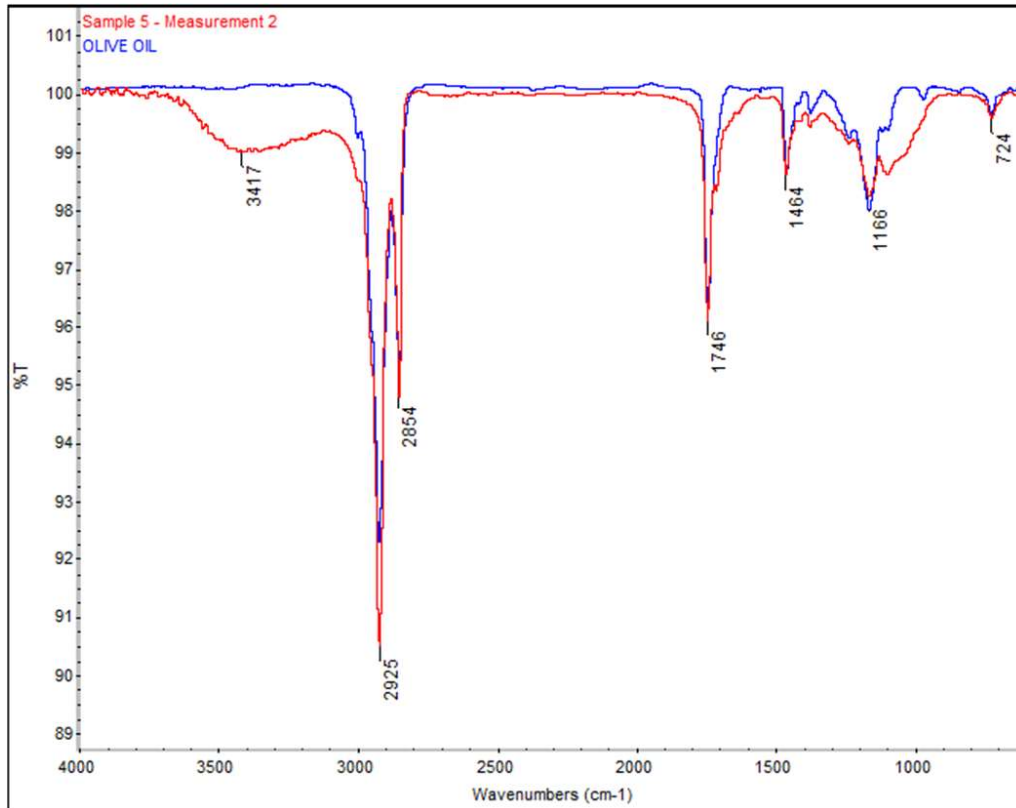
# Do you know your microplastics?



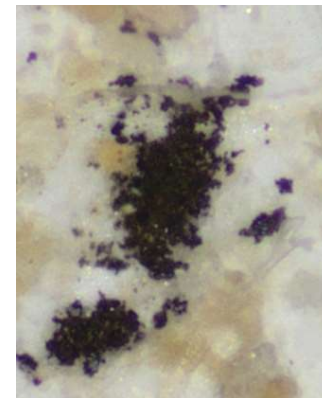
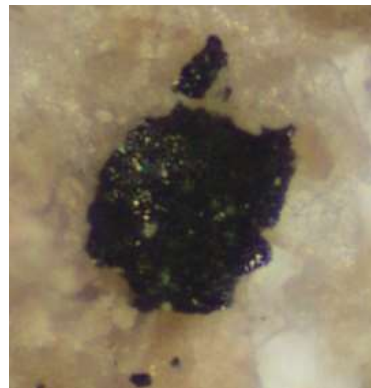
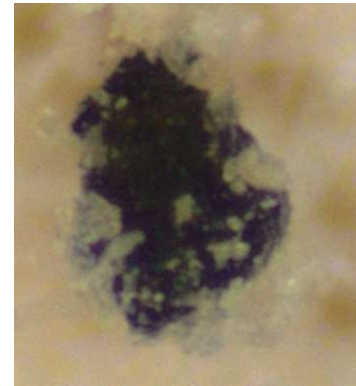
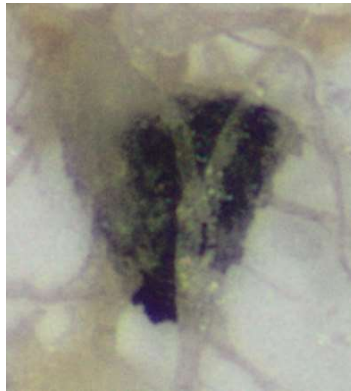
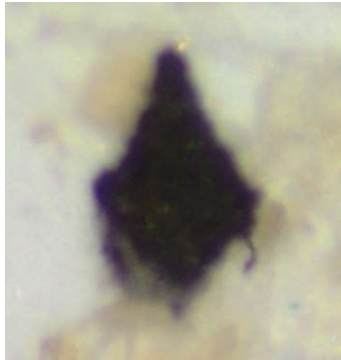
# Confirmed as polyethylene



# Mixture of polystyrene and olive oil



# Unidentified Black Objects (UBO)



# Report format

Sample ID: \_\_\_\_\_  
Sampling Site: \_\_\_\_\_

Sampling Date: \_\_\_\_\_  
Extraction Date: \_\_\_\_\_  
Analysis Date: \_\_\_\_\_

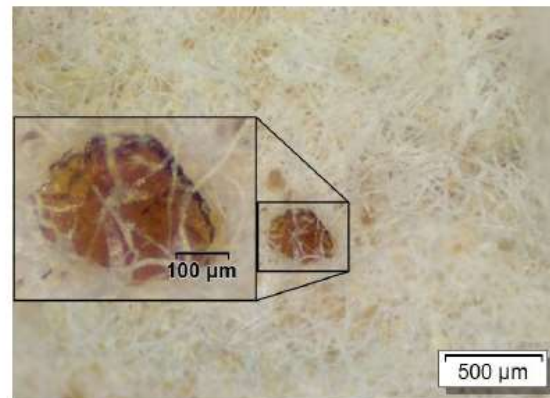
## Microscopy Report



Sieve size: 125 µm 355 µm 1,000 µm  
☐ ☐ ☐

Particle type: Fragment Pellet Fiber  
☐ ☐ ☐  
Film Foam Other  
☐ ☐ ☐

Comments: \_\_\_\_\_  
\_\_\_\_\_



Sieve size: 125 µm 355 µm 1,000 µm  
☐ ☐ ☐

Particle type: Fragment Pellet Fiber  
☐ ☐ ☐  
Film Foam Other  
☐ ☐ ☐

Comments: \_\_\_\_\_  
\_\_\_\_\_



# The assignment – revisited

To characterize and quantify microplastics in wastewater effluent

- ▶ BACWA microplastics workgroup goal
  - Routinely performed – **No**
    - Not too expensive – **No**
    - Not too complex – **No**
  - Robust QA/QC criteria – **Need to be developed**
  - Reproducible – **Need a method to test this concept**
  - Complete documentation and transparency – **Yes**
  - Provide useful information for decision making – **Yes/Not yet**
- ▶ Evolving definition:  
*Material that passes through a 5mm sieve but retained by 0.125 mm sieve; withstands oxidation step, **withstands hexane rinses**, .... and then confirmed as plastic.*



# Lessons learned

- ▶ Sampling method, duration, time of day likely influences results – if reported as particles/day
- ▶ Handling microplastics may destroy them or makes many out of one
- ▶ Visual identification is unreliable. Results will remain as subjective interpretation unless confirmed by FTIR – for individual particle counting
- ▶ Microbeads contribution to wastewater microplastics profile is very small



# Recommendations for next steps

- ▶ Define microplastic
- ▶ Standardized, reliable, reproducible method needed for making comparisons or decisions
- ▶ Report as a concentration rather than particle count when appropriate
- ▶ Report a weight rather than particle count
- ▶ Method defined parameter
- ▶ Maintain impeccable documentation
- ▶ Develop a method through 'Standard Methods' process



# Acknowledgement

- ▶ BACWA lab committee microplastics workgroup (in alphabetical order of agency name)
  - CCCSD: Jim Wan
  - EBMUD: Artem Dyachenko, Jason Mitchell
  - Hayward: Farid Remezanzadeh
  - San Jose: Noel Enoki
  - SFPUC: Ken Lee
  - Union Sanitary District: Guy Moy



## ► Questions

